Research Article

Hüseyin Ovalioglu*

Sample age effect on parameters of dynamic nuclear polarization in certain difluorobenzen isomers/MC800 asphaltene suspensions

<https://doi.org/10.1515/chem-2021-0114>

received November 22, 2021; accepted December 7, 2021

Abstract: Because of magnetic spin–spin interactivity between ^{19}F nucleus of the solvent and delocalized electrons on the MC800 asphaltene, the Overhauser dynamic nuclear polarization (DNP) method is able to give a substantial boost in the signal acquired from studies focused on nuclear magnetic resonance (NMR). The suspensions of asphaltene in difluorobenzene isomers were studied using Overhauser effect type DNP and NMR investigations at room temperature in a small magnetic field of 1.53 mT. The used asphaltene was obtained from MC800 liquid asphalt from Heavy Iran. Each sample of the solvent medium was produced at three different concentrations of asphaltene. These samples were stored in the refrigerator for 7 years, until DNP parameters were found by new DNP tests. As a result, the influence of sample age on parameters of DNP was studied, and then the findings were analyzed.

Keywords: difluorobenzene, asphaltene, dynamic nuclear polarization, Overhauser effect

1 Introduction

Asphaltene is the heaviest and most viscous aromatic component of crude oil. It is also the most polar component, being soluble in aromatic solvents such as toluene and xylene but insoluble in normal aliphatic hydrocarbons such as *n*-heptane and *n*-hexane [1–3]. Asphaltene precipitates only when unstable. Its stability is affected by different parameters, including the pressure, temperature, and characteristics of crude oil mixtures [4,5].

Asphaltenes, are a part of petroleum, are considered to be polar species, have greater aromatic complexes, and consist of heteroatoms (e.g., O, S, and N), alkyl chains, and certain metals [6]. Asphaltenes have unpaired electrons, which are observed in crude petroleum by using the electron spin resonance (ESR) experiments [7].

Dynamic nuclear polarization (DNP) uses liquid state interactions between nucleus and unpaired electron spins to produce enhanced nuclear polarization after the saturation of ESR radical transitions. The maximum DNP enhancement rate of the nuclear magnetic resonance (NMR) signal is calculated by the electron-to-nuclear gyromagnetic ratio, γ_e/γ_n . For ^{19}F spin, this ratio is 700.

It becomes apparent that studies of the coupling between I, nuclear spin reservoir, and S, electronic spin reservoir, may put forward an insight into the dynamics and structure of these sophisticated materials. The magnetic interaction, which is the source of DNP, between the nucleus and unpaired electron, is much stronger than the inter-nuclear interaction experienced in broad solvent region. The intensities and spectral densities of the inter-molecular scalar could arise from direct contact between the solvent nuclei and unpaired electrons of the radical or from a temporary overlap of the delocalized molecular orbitals during the diffusion process [8–10]. The Overhauser dynamic nuclear polarization type mechanism (ODNP) for the hyperpolarization should be the most efficient as crude oil is historically treated as a viscous liquid [11]. As the comparatively high mobility of oil molecules, including radicals, requires an appropriate regulation of electron–nuclear interaction, this condition leads to an efficient propagation of polarization between nuclei and electrons in oil. The main aspect of ODNP is that when the microwave pumping frequency is in precisely the same resonance as the EPR transition, the full effect of electron polarization conversion on the nuclear system is obtained. In fact, as early as the 1950s, Poindexter [12,13] recorded Overhauser form of DNP in the external magnetic field $B_0 = 18\text{ G}$ on protons of “light” or “medium” crude oils that have a viscosity of 25–40 mPa s.

* Corresponding author: Hüseyin Ovalioglu, Physics Department, Faculty of Arts and Sciences, Bursa Uludag University, 16059, Bursa, Turkey, e-mail: ovali@uludag.edu.tr

The nuclear spins are the ^{19}F spins in this sample, and they are the ^{19}F center of the solvent medium, whereas the electron spins are the free electrons on the asphaltene micelles. Unpaired electrons have been dislocated to the unfilled carbon bonds of asphaltene particles compact aromatic structure [14]. We revealed a dipolar interaction between the solvent fluorine atoms and unpaired colloidal asphaltene electrons through the DNP process. In a low magnetic field, electron spin saturation, as well as DNP improvements, were achieved, and also DNP parameters have been determined.

This study aimed to investigate the DNP parameters (A_∞ , U_∞ , ρ , f , s , and K) of difluorobenzene isomer solvents in MC800 asphaltene free radical against time at room temperature at 1.53 mT low magnetic field.

2 Theory

The whole DNP phenomenon theory through the Overhauser effect in free radicals solutions has already been published in the technical literature [15–20]; thus, in this article, we present just a short overview of the theory that applies to our study. In Figure 1, a schematic display of a 1/2-spin and a two-spin electron system energy level is displayed. In this figure, m_s and m_I are, respectively, electron and nucleus magnetic quantum numbers.

The possibilities of transition through relaxation may be determined in this system as follows (Table 1).

Here, $w_1 = w'_1 + w''_1 \cdot 2w'_1$ corresponds to the transition probability owing to spin coupling of nuclear electron, and $2w''_1$ denotes the probability of transition because of various processes of relaxation.

An expression for the motion equation of nuclear polarization (NP) is given as [21].

Figure 1: Diagram showing the energy level of a nucleus that has a 1/2-spin and two-spin electron system. m_I and m_s denote the magnetic quantum numbers of nucleus and electron, respectively. ω_i and w_i ($i = 0, 1, 2$) represent the transition frequencies and probabilities. Here ω_S/ω_I equals to 700 for ^{19}F nucleus.

Table 1: Chart of determination of transition probabilities via relaxation

	$m_s m_I$	$m_s m_I$	
w_0	$ +-\rangle \Leftrightarrow +-\rangle$	$ +-\rangle \Leftrightarrow +-\rangle$	Flip-flop (with the frequency $\omega_S + \omega_I$)
w_2	$ ++\rangle \Leftrightarrow --\rangle$	$ --\rangle \Leftrightarrow ++\rangle$	Flip-flop (with the frequency $\omega_S - \omega_I$)
w_1	$ \pm-\rangle \Leftrightarrow \pm+\rangle$	$ \pm+\rangle \Leftrightarrow \pm-\rangle$	$m_s = \text{constant}$ (with the frequency ω_I)

$$\frac{dP_z}{dt} = -(\omega_0 + 2\omega_1 + \omega_2) \left[(P_z - P_0) - \frac{\omega_2 - \omega_0}{\omega_0 + 2\omega_1 + \omega_2} (\Pi_z - \Pi_0) \right] \quad (1)$$

Π_z and P_z indicate the unpaired electron spins and the NP of the nuclear spins. P_0 and Π_0 are the thermal equilibrium polarizations.

$T_1^{-1} = \omega_0 + 2\omega_1 + \omega_2$ correspond to the overall rate of relaxation of the nuclear spin-lattice, and $f = (\omega_0 + 2\omega'_1 + \omega_2)/[\omega_0 + 2(\omega'_1 + \omega''_1) + \omega_2]$ stands for the leakage factor, which reveals the degree of efficiency that electron spins relax nuclear spins. The above-mentioned leakage factor is ranging from 0 (no nuclear–electron coupling relaxation) and 1 (there is not any other relaxation mechanisms). $\rho = (\omega_2 - \omega_0)/(\omega_0 + 2\omega'_1 + \omega_2)$ stands for the coupling factor of nuclear–electron that relies on the type of nuclear–electron interactivity. Here, ρ may range between +0.5 that corresponds to purely dipolar interactivities and −1 that corresponds to purely scalar interactivities. Finally, $s = (\Pi_0 - \Pi_z)/\Pi_0$ represents the saturation factor equivalent to 1 ($0 \leq s \leq 1$) in full EPR saturation.

At the steady state, namely, $dP_z/dt = 0$, the formulation of Overhauser enhancement factor is as follows:

$$A = \frac{P_z - P_0}{P_0} = -\rho f s \left| \frac{\gamma_S}{\gamma_I} \right|. \quad (2)$$

Here, γ_I and γ_S correspond to the gyromagnetic ratios of nucleus and electron in turn ($\gamma_I > 0$; $\gamma_S < 0$).

In the event that the saturation state is met, the reciprocal of the enhancement factor is demonstrated below which is extrapolated for infinite ESR power,

$$\left(\frac{P_z - P_0}{P_0} \right)^{-1}_{s \rightarrow 1} \rightarrow A_\infty^{-1}. \quad (3)$$

There, f , leakage factor can be formulated as follows:

$$f = \frac{T_1'^{-1}}{T_1^{-1}} = \frac{T_1'^{-1}}{T_1'^{-1} + T_{10}^{-1}} \quad (4)$$

Here, $T_1'^{-1} = \omega_0 + 2\omega'_1 + \omega_2$ denotes the rate of nuclear relaxation as a result of coupling of nuclear–electron, and $T_{10}^{-1} = T_1'^{-1} = 2\omega''_1$ is the rate of nuclear relaxation

caused by other processes. The leakage factor reciprocal is denoted as follows:

$$f^{-1} = 1 + \frac{T_{10}^{-1}}{T_1'^{-1}}, \quad (5)$$

$T_1'^{-1}$ is proportionate to c , the concentration of electron spin (or free radical), alternatively. In this way, equation (3) puts forward

$$A_{\infty}^{-1} = \left(1 + \frac{T_{10}^{-1}}{kc}\right) \left(-\rho \left|\frac{\gamma_S}{\gamma_I}\right|\right)^{-1}. \quad (6)$$

Here, the ultimate electron spin concentration is as follows:

$$(A_{\infty}^{-1})_{f \rightarrow 1, c \rightarrow \infty} \rightarrow \left(-\rho \left|\frac{\gamma_S}{\gamma_I}\right|\right)^{-1} = U_{\infty}^{-1}. \quad (7)$$

Since, $|\gamma_S/\gamma_I| = +700$ for ^{19}F , equation (7) presents

$$\rho = -U_{\infty}/700. \quad (8)$$

In the white spectral region, namely in extreme narrowing case ($\omega_S t_f \ll 1$). In addition, an earlier study [22] denotes the K parameter that describes the relative significance of both scalar and translational dipolar interactivities,

$$K = \frac{2}{15} \frac{J_{sc}(0)}{J_I^D(0)}. \quad (9)$$

Here, $J_I^D(0)$ and $J_{sc}(0)$ equal to the translational and scalar dipolar spectral density functions. Finally, K is computed by using the experimental ρ value at high temperatures and in weak fields [19,23,24] as follows:

$$K = \frac{1 - 2\rho}{1 + \rho}. \quad (10)$$

3 Methods

3.1 Solvents and asphaltene

MC-800 liquid asphalt is used to obtain the asphaltene. The asphalt is dissolved in a tenfold excess volume of benzene and precipitated in a further tenfold excess volume of petroleum ether at a boiling temperature interval of 40 and 60°C (namely 1-volume asphalt, 10-volume benzene, and 100-volume petroleum ether) [25,26]. Filtration was used to collect the precipitate, which was then dried. The resultant was a black semisolid asphaltene. Asphaltene made up 14% of the weight of MC-800 liquid asphalt.

The solvents were obtained from Fluka (Switzerland) and Aldrich Chem. Co. (USA) and utilized exactly as they were supplied. The purities, viscosities, molecular weights,

Table 2: NMR sensitivities and basic constants of the solvents chosen

Solvent	Molecular weight (g/mol)	Melting point (°C)	Boiling point (°C)	Density (g/cm ³)	Viscosity (cP)	Dipole moment (D)	NMR sensitivity (×10 ²² spin/cm ³)
<i>o</i> -Difluorobenzene (C ₆ H ₄ F ₂)	114.09	−34	92	1.158	0.548	2.40	1.22
<i>m</i> -Difluorobenzene (C ₆ H ₄ F ₂)	114.09	−59	83	1.163	0.603	1.50	1.23
<i>p</i> -Difluorobenzene (C ₆ H ₄ F ₂)	114.09	−13	88–89	1.514	0.608	0	1.24

Figure 2: Structure of 1,2 difluorobenzene (ortho), 1,3 difluorobenzene (meta), and 1,4 difluorobenzene (para) molecules (green color “fluorine,” blue color “hydrogen,” and gray color “carbon”).

boiling temperatures, freezing temperatures, densities, dipole moments, and their computed NMR sensitivities of the chosen solvents are reported in Table 2. Figure 2 depicts the molecular structures of these solvents.

3.2 Preparation of the samples

The samples had been produced at three distinct degrees of radical concentration. The samples were sealed Pyrex tubes (18 mm diameter and resistant to liquid nitrogen temperature) after being degassed by means of minimum five freeze–pump–thaw cycles that uses liquid nitrogen at about 10^{-5} Pa in a Leybold–Heraeus vacuum system. Figure 3 demonstrates how the samples were degassed and sealed in Pyrex tubes. The degassing process is required because the presence of oxygen in the sample prevents the EPR transition from being easily stimulated. To the naked eye, the solutions look substantially identical, as there is no apparent indication of fast flocculation.

3.3 Asphaltene characterization

The tests have been conducted in a low energy field, NMR spectrometer with double resonance, operating at 1.53 mT. The continuous-wave technology spectrometer has a resonance frequency of 45.5 MHz for electrons and 61.2 kHz for nucleus of ^1H . That field is generated by a coil system of Helmholtz that is supplied with a 2 A current. Within 10^{-6} A, the magnet current is stabilized. To get a high signal-to-noise ratio, the field must also be very homogenous in terms of time and space. The signals have been detected using an amplitude modulation method and amplified in a low frequency and narrow-band amplifier, which is linked to a phase-sensitive detector (or lock-in detector) and a recorder. A digital sweep generator

sweeps the external magnetic field [27]. The spectrometer also includes an automated temperature management mechanism that works with either liquid nitrogen vapor or hot airflow. Earlier studies also detailed the spectrometer [27–29].

The observations on the NMR pure and double resonance signals, each with signal intensity P_o and P_z , are considered in this spectrometer. The standard approach of amplification modulation produces the signals of the central bands, and also the first and second side bands. The P_o and P_z values of the central band derivatives were considered to represent peak-to-peak values.

In the liquid phase, the saturation tests were conducted with an accuracy of $\pm 2^\circ\text{C}$. In each sample, P_o was measured four-times at three distinct levels and at a room temperature of $25 \pm 2^\circ\text{C}$, and P_z from five distinct ESR power values were acquired to saturate the electronic spin polarization. Moreover, the radio frequency signal was received from the Rohde & Schwarz sml 01 signal generator within the ESR coil’s frequency range of 25–60 MHz

Figure 3: The sample is degassed and sealed in Pyrex tubes.

and were amplified with a T&C Power Conversion LA-50 HF amplifier.

3.4 Setting the DNP Parameters

To calculate the A_∞ values, the reciprocal of the enhancement factor (namely $[(P_z - P_0)/P_0]^{-1}$) should be derived as a function of the ESR power's reciprocal value. In this context, ESR power is proportionate to either H_{le}^{-2} or V_{eff}^{-2} , where V_{eff} value represents the high frequency voltage on the ESR coil. For complete ESR saturation, Π_z value will be zero, and the saturation factor (s) will come close to 1. The ESR power needs to reach ∞ , or V_{eff}^{-2} to 0, in order to achieve complete saturation. Therefore, the A_∞^{-1} value in the linear graph is equal to the junction of the extrapolated best-fit line and $V_{eff}^{-2} = 0$ line. Figure 4 depicts variation of $-[(P_z - P_0)/P_0]^{-1}$ vs V_{eff}^{-2} for three concentrations of asphaltene/fluorobenzene samples. The A_∞^{-1} values are the intersections of the $V_{eff}^{-2} = 0$ line and the best suited extrapolated line. Figure 4 demonstrates the R^2 values to assess the consistency between the experimental points and the linear fit function. A maximum inaccuracy of approximately $\pm 10\%$ is found for a single point in the graphic.

In Figure 5, as A_∞^{-1} values proportionate to the reciprocal concentration of asphaltene c^{-1} , the ultimate enhancement factor U_∞ may be calculated simply. The U_∞^{-1} values are the junction points on the best-fit extrapolated lines and $c^{-1} = 0$ line ($f = 1, \infty$ concentration).

After U_∞ is determined, the nuclear–electron coupling parameter value ρ may be derived by using equation (8).

The A_∞/U_∞ ratio that is calculated from equations (3) and (7) is used to achieve f value for each of the concentrations. Finally, by using the equations (2) and (3), the s value was attained from the enhancement factor A_{end} for the maximum existing ESR power divided by A_∞ .

4 Results and discussion

4.1 EPR Spectra

To evaluate DNP parameters in the magnetic field, a free radical EPR spectrum is necessary. The solvents should not influence the ESR spectrum [19]. The EPR spectrum obtained in this study and the spectrum EPR produced by Kirimli and Ovalioglu [30] are displayed in Figure 6. The spectrum produced for asphaltene/meta-difluorobenzene at a 3.10 kg/m^3 concentration is optimally matched to observed values by a Gaussian, as shown in the Figure 6, and the resultant fit may be described by the following equation:

$$y = A \cdot e^{\left[-\frac{1}{2} \frac{(x-x_c)^2}{\sigma^2} \right]}. \quad (11)$$

The spectrum was portrayed as a single Gaussian generated via the superposition of several Lorentzians. Additionally, the measured values of these concentrations are fit with Gaussian functions given by the following equations:

$$-\frac{P_z - P_0}{P_0} = 0.856 \exp \left[-\frac{(v_s - 45.51)^2}{102.97} \right]. \quad (12)$$

Figure 4: Variation of $\left[\frac{(P_z - P_0)}{P_0} \right]^{-1}$ versus V_{eff}^{-2} for asphaltene/fluorobenzene derivative samples at three distinct concentration levels. Here, A_∞^{-1} values equivalent to the junction points of the extrapolated best-fit and the $V_{eff}^{-2} = 0$ lines. (The red lines represent 1,4-difluorobenzene, the blue lines represent 1,3-difluorobenzene, and the green lines represent 1,2-difluorobenzene.) (a) Ref. [30] Data and (b) 2021 data.

Figure 5: Instances of the evaluations for ultimate enhancement factor at room temperature. Here, the U_∞^{-1} values are equivalent to the junction points of extrapolated best-fit lines and the $c^{-1} = 0$ line (ref. [30] 2014 and 2021 data).

Figure 6: The EPR spectrum acquired in the study (□) and Kirmli's EPR spectrum (2014) (Δ) [30].

4.2 DNP parameters

DNP parameters (A_∞ , U_∞ , ρ , f , s , and K) were attained again after 7 years, and the data obtained are listed in Table 3 and compared with previous data [31].

Experimental saturations range from 78 to 96%. All A_∞ and U_∞ parameters have negative values as P_z and P_0 NMR signals are opposite to each other. The value of A_∞ varies between -3.7 and -5.6 . As a result, the dipole–dipole interactivity is dominant in the intermolecular

spin–spin interactivity, which is proportionate to $1/r^3$. The reciprocal cube of the distance between the suspended fluid medium's fluorine spins and the delocalized unpaired electron spins on the partial carbon bonds of the asphaltene micelles' concentrated aromatic structure. The smallest ρ is obtained for the MC800 asphaltene/para-difluorobenzene asphalt suspensions. Here, all of the suspensions have positive ρ values, which shows that the dipolar interactivity is predominant. For difluorobenzene isomer solvents, the K parameters obtained through equation (10) range between 0.970 and 0.978. In this equation, smaller ρ values correlate to the greater K values and therefore make scalar interactivities more efficient. This shift in ρ with solvent indicates that a tighter touch takes place while natural resins arising from the asphaltene surface sections are peeled away. For a very short period, the molecules of the solvent may bind to the particles of colloidal asphaltene, namely liquid asphaltene, creating complexes and establishing scalar interactivities with a correlation period τ_{sc} . For the same sample, specific solvent molecules are able to diffuse in and out of the asphaltene micelles while participating in dipolar interactivities with a correlation period τ_d . Molecules of the solvent linked to the colloid follow the rotating model, whereas the solvent molecules not connected to the colloid follow the diffusion model [19]. In addition to the geometric distances,

Table 3: DNP parameter values for the difluorobenzene isomer suspensions with MC800 asphaltene

2021 data							
Solvent medium	c (kg/m ³)	A_∞	U_∞	ρ	f	s	K
1,2 Difluorobenzene (C ₆ H ₄ F ₂)	1.8	−3.8	−7.1	0.010	0.539	0.959	0.970
	3.2	−4.			0.696	0.917	
	6.1	−5.6			0.790	0.914	
1,3 Difluorobenzene (C ₆ H ₄ F ₂)	1.6	−3.7	−6.5	0.009	0.575	0.929	0.973
	3.1	−4.6			0.707	0.901	
	6.1	−5.3			0.818	0.886	
1,4 Difluorobenzene (C ₆ H ₄ F ₂)	1.8	−3.7	−5.2	0.007	0.712	0.784	0.978
	3.28	−4.3			0.814	0.910	
	6.18	−4.7			0.897	0.934	
2014 data [30]							
Solvent medium	c (kg/m ³)	A_∞	U_∞	ρ	f	s	K
1,2 Difluorobenzene (C ₆ H ₄ F ₂)	1.8	−4.6	−8.1	0.012	0.568	0.940	0.947
	3.2	−5.7			0.710	0.929	
	6.1	−6.6			0.814	0.931	
1,3 Difluorobenzene (C ₆ H ₄ F ₂)	1.6	−4.7	−7.7	0.011	0.606	0.913	0.949
	3.1	−5.6			0.723	0.912	
	6.1	−6.5			0.846	0.906	
1,4 Difluorobenzene (C ₆ H ₄ F ₂)	1.8	−4.6	−6.4	0.009	0.712	0.768	0.962
	3.28	−5.1			0.804	0.908	
	6.18	−5.8			0.904	0.828	

the closest effective distance among the interacting spins relies on the relocation of unpaid electrodes in the micelles of the asphaltene [19].

The DNP factor is varies with the concentration. When the interactivities are weak, f becomes close to zero, and although the interactivities are strong, f equals to one. The rise in A_∞ is proportional to the increase in concentration.

The atom substituents of fluorine are found in the solvent molecules. ρ fluctuates in the range of 0.007 and 0.010 as the count of fluorine atoms in fluorobenzene derivatives with strongly electronegative [32] substituents such as $-f$ increases. These substituents that contain fluorine atoms were observed to have signal enhancement. For this reason, interactivities of the difluorobenzene isomers that contain asphaltene behave neither purely dipolar nor scalar. However, the $-f$ substituents alter the benzene ring's chemical environment in a more effective way. With respect to the pure dipole-dipole interactivities for protons and a variety of scalar interactivity degrees of fluorine, the polarization level of ^{19}F was linked to the molecular characteristics of fluorocarbon solvents [33].

If a single fluorine substituent is located in a better location in a molecule, it may affect the physical and chemical characteristics of the molecule significantly. In the literature, there are many researches about the effect of fluorine on the chemical and physical characteristics for compounds. Probably, ^{19}F is the nucleus that is examined most in NMR after carbon and hydrogen due to its magnetic features and the significance of molecules consist of fluorine. Some of the advantages of the ^{19}F nucleus are as follows: it is plentiful in the nature with a 100% purity, its spin value is $I = 1/2$, and it has a high-level magnetogyric ratio that is equivalent to 0.94 of the magnetogyric ratio of ^1H [34].

5 Conclusion

The following results are obtained as a result of the experimental study that is conducted in line with the aim of this study.

To study colloidal suspensions solvent mediums of MC800 asphaltene consisting of 1,2 difluorobenzene, 1,3 difluorobenzene, and 1,4 difluorobenzene. Overhauser affect type DNP method is utilized at room temperature in a 1.53 mT low-level magnetic field. For testing environment, at each solvent medium sample, three different concentrations of asphaltene was used. Consequently, there were nine samples in total. In the EPR spectrum

of the asphaltenes, the spectrum of MC800 asphaltene in the 1,3 difluorobenzene solvent medium was discovered to be a single Gaussian peaking about 45.5 MHz. The pattern of the EPR spectrum agrees well with findings of Kirimli's study (2014) [30].

In the study, ρ value, namely the nuclear-electron coupling parameter, was observed to be lower after samples that had produced a colloidal 1,2 difluorobenzene, 1,3 difluorobenzene, and 1,4 difluorobenzene solvent media of MC 800 asphaltene for 7 years. The nuclear-electron coupling parameter ρ ranges between pure dipolar value of +0.5 and pure scalar value of -1.0 in low magnetic fields, and the new ρ values discovered to be within these limits. In our experimentation, new ρ values are found to be positive, which suggests that the dipolar portion in spin-spin interactivities is prevalent. K value depicts the significance of almost all the samples according to the scalar coupling parameter. In other words, in awaited samples, the scalar section of the intermolecular spin-spin interactivities rises, and the dipolar section of the interactivities diminishes. For the 1,4 difluorobenzene solution medium, the lowest absolute U_∞ value (thus, ρ value as well) has been achieved. This suggests that the asphaltene has been much more efficiently dispersed and suspended by 1,2-difluorobenzene and 1,3-difluorobenzene. In other respects, in terms of electrical dipole moment value, the 1,4 difluorobenzene has the lowest value.

We think that in biological samples, comprehensive information about the chemical environment may be acquired using free radicals and aromatic fluorinated solvents that are predisposed to the scalar interactivity in EPR oximetry, which is promoted through the Overhauser effect [31,35].

This research makes a positive contribution to the study of the asphaltene surface and aids related research with DNP findings. Furthermore, DNP investigations are helpful applications for the empirical characterization of asphaltene solutions.

Funding information: This study was supported by the Research Fund of the Uludag University, Project Number OUAP(F)-2012/30. The authors thank to Uludag University for financial support.

Conflict of interest: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the study reported in this article.

Ethical approval: The conducted research is not related to either human or animal use.

Data availability statement: In this article, it is okay to use Figures 5 and 6, quoted from reference [30], of which I am the author.

References

- [1] Mahmood MSA, Hamad AAL-L. Synthesis and characterization of tannic acid esters and their performances as asphaltene dispersants. *J Pet Sci Eng.* 2021;201:1–9.
- [2] Alrashidi H, Afra S, Nasr-El-Din HA. Application of natural fatty acids as asphaltene solvents with inhibition and dispersion effects: a mechanistic study. *J Pet Sci Eng.* 2019;172:724–30.
- [3] Campen S, Moorhouse SJ, Wong JS. Mechanism of an asphaltene inhibitor in different depositing environments: influence of colloid stability. *J Pet Sci Eng.* 2020;184:106502.
- [4] Junior LCR, Ferreira MS, da Silva, Ramos AC. Inhibition of asphaltene precipitation in Brazilian crude oils using new oil soluble amphiphiles. *J Pet Sci Eng.* 2006;51(1–2):26–36.
- [5] Vargas FM, Creek JL, Chapman WG. On the development of an asphaltene deposition simulator. *Energy Fuels.* 2010;24(4):2294–9.
- [6] Evdokimov IN, Eliseev NY, Akhmetov BR. Asphaltene dispersions in dilute oil solutions. *Fuel.* 2006;85(10–11):1465–72.
- [7] Gutowsky HS, Roger Ray B, Rutledge RL, Unterberger RR. Carbonaceous free radicals in crude petroleum. *J Chem Phys.* 1958;28:744–5.
- [8] Shukla AK. Analytical characterization methods for crude oil and related products. Hoboken NJ: JohnWiley & Sons Ltd; 2018.
- [9] Martyanov ON, Larichev YV, Morozov EV, Trukhan SN, Kazarian SG. The stability and evolution of oil systems studied via advanced methods in situ. *Russian Chem Rev.* 2017;86:999–1023.
- [10] Sapunov V, Denisov A, Saveliev D, Soloviev A, Khomutov S, Borodin P, et al. New vector/scalar Overhauser DNP magnetometers POS-4 for magnetic observatories and directional oil drilling support. *Magnetic Reson Solids.* 2016;18(2):16209.
- [11] Pradhan A, Ovalles C, Moir M. Characterization of heavy petroleum fractions by NMR techniques. Ovalles C, Moir M, Eds *The Boduszynski continuum: contributions to the understanding of the molecular composition of petroleum.* Washington, DC: ACS Symposium Series OUP; 2018. p. 73–86.
- [12] Poindexter E. An overhauser effect in natural crude oil. *Nature.* 1958;182:1087.
- [13] Poindexter EH, Torrey HC. Overhauser effect well logging. U.S. Patent, US 3096476A, 1963.
- [14] Griesinger C, Bennati M, Vieth HM, Luchinat C, Parigi G, Hofer P, et al. Dynamic nuclear polarization at high magnetic fields in liquids. *Prog Nucl Magnetic Reson Spectrosc.* 2012;64:4.
- [15] Abragam A. The principles of nuclear magnetism. Chapter 8. Oxford, UK: Oxford University Press; 1961.
- [16] Hausser KH, Stehlik D. Dynamic nuclear polarization in liquids. *Adv Magnetic Optical Reson.* 1968;3:79–139.
- [17] Armstrong BD, Soto P, Shea JE, Han S. Overhauser dynamic nuclear polarization and molecular dynamics simulations using pyrroline and piperidine ring nitroxide radicals. *J Magnetic Reson.* 2009;200:137–41.
- [18] Potenza J. Measurement and applications of dynamic nuclear polarization. *Adv Mol Relax Process.* 1972;4:229–354.
- [19] Müller-Warmuth W, Meise-Gresch K. Molecular motions and interactions as studied by dynamic nuclear polarization (DNP) in free radical solutions. *Adv Magnetic Optical Reson.* 1983;11:1–45.
- [20] Slichter CP. Principles of magnetic resonance. Berlin: Springer; 1989.
- [21] Kramer KD, Müller-Warmuth W. Über Zusammenhänge der Overhauser-Kernpolarisation mit der Molekülbewegung, der Frequenz und der Relaxation in Flüssigkeiten. *Z Naturforschung.* 1964;19a:375.
- [22] Muller-Warmuth W, Oztekin E, Vilhjalmsen R, Yalciner A. Dynamic polarization, molecular motion and solvent effects in several organic solutions as studied by proton-electron double resonance. *Z für Naturforschung A.* 1970;25:1688–95.
- [23] Peksoz A, Cimenoglu MA, Yalciner A. Dynamic nuclear polarization in some aliphatic and aromatic solutions as studied by fluorine-electron double resonance. *J Dispers Sci Technol.* 2008;29:40–5.
- [24] Kirimli HE, Peksoz A. A low field proton–electron double resonance study for paramagnetic solutions. *Mol Phys.* 2011;109:337–50.
- [25] Poindexter EH. Dynamic nuclear polarization and molecular aggregation in asphaltene suspensions. *J Colloid Interface Sci.* 1972;38(2):412–23.
- [26] Gulsun Z, Yalciner A. Dynamic nuclear polarization in colloidal asphaltene suspensions. *Commun Faculty Sci Univ Ank.* 1980;29:1–17.
- [27] Akay C, Yalciner A. A new weak field double resonance NMR spectrometer. *Z für Naturforschung A.* 1995;50:177–85.
- [28] Yalciner A. ESR hyperfine structure of α , γ -Bisdiphenylene- β -phenyl allyl via overhauser effect in weak magnetic fields. *Commun Faculty Sci Univ Ank.* 1978;27:1–20.
- [29] Yalciner A. Dynamische Kernpolarisation und Substituenteneinflüsse auf Zwischenmolekulare Wechselwirkungen in Lösungen Freier Radikale. PhD thesis. Ankara, Turkey and Mainz, Germany: Ankara University and Max-Planck Institute; 1970.
- [30] Kirimli HE, Ovalıoglu H. ¹⁹F Dynamic nuclear polarization and SEM in suspensions consisting of fluorobenzene derivatives and asphaltene extracted from MC-800 liquid asphalt. *J Dispers Sci Technol.* 2014;35:255–64.
- [31] Murugesan R, English S, Reijnders K, Yamada K, Cook JA, Mitchell JB, et al. Fluorine electron double resonance imaging for ¹⁹F MRI in low magnetic fields. *Magn Res Med.* 2002;48:523–9.
- [32] Yalciner A, Cimenoglu MA, Akay C, Ovalıoglu H. Dynamic nuclear polarization in suspensions of liquid asphalts in weak magnetic field. *ARI—An Interdiscip J Phys Eng Sci.* 1998;51:141–4.
- [33] Potenza JA, Poindexter EH. Contribution from the institute for exploratory research, U.S. Army Electronics Command, Fort Monmouth, NJ, USA; 1968.
- [34] Vilcachagua JD, Ducati LC, Rittner R, Contreras RH, Tormena CF. Experimental, SOPPA(CCSD), and DFT analysis of substituent effects on NMR ¹JCF coupling constants in fluorobenzene derivatives. *J Phys Chem A.* 2011;115:1272–9.
- [35] Guiberteau T, Grucker D. Dynamic nuclear polarization imaging in very low magnetic fields as a noninvasive technique for oximetry. *J Magn Reson.* 1997;124:263–6.